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(54) **Aqueous inks**

(57) An aqueous ink comprises water and a polyhydric alcohol as an aqueous medium which contains a colourant and a lubricating additive selected from fluoro-surfactants, water-soluble silicone oils and mixtures thereof. An aminotrimethylenephosphonic acid alkali metal salt may also be included.

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FIG. 1

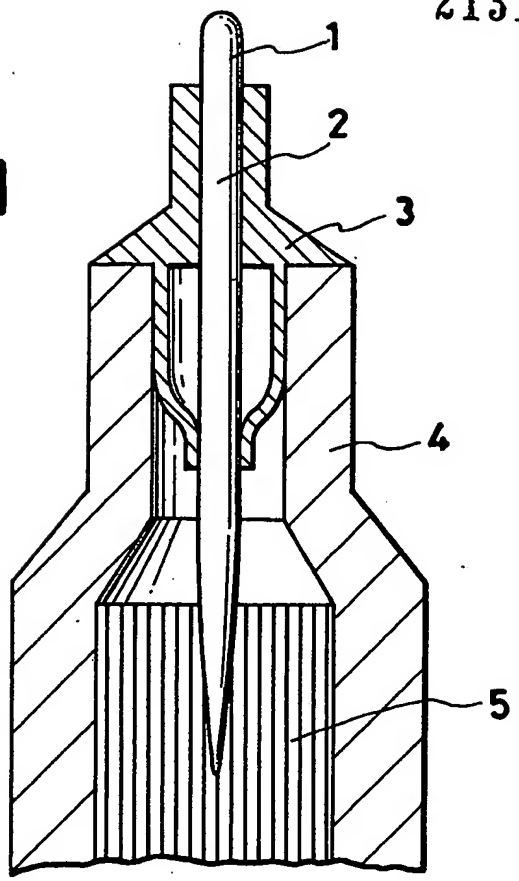
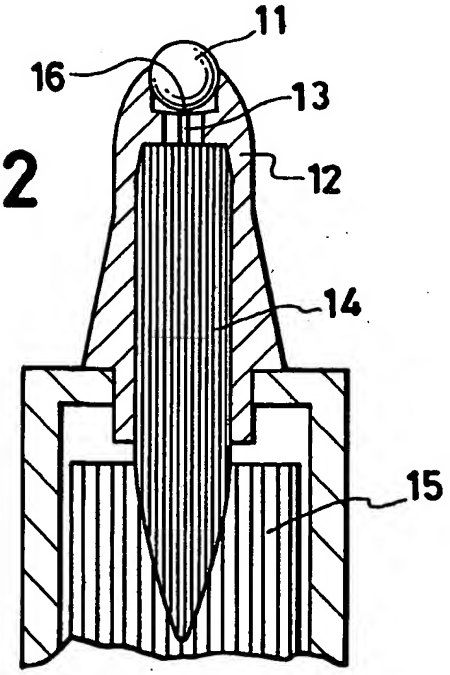


FIG. 2



SPECIFICATION

Aqueous inks

This invention relates to aqueous inks of the type suitable for use in ball-point pens, felt-tip pens, fountain pens, and in ink-jet printing.

Conventional aqueous inks comprise a water-miscible solvent and a dye or pigment dissolved or dispersed therein. Writing utensils, in use with such inks, tend to squeak when drawn over writing paper, to scratchiness, and to produce characters which are of uneven density, and may suffer a cut-off in satisfactory ink supply. Further, in a ball-point pen in which a conventional aqueous ink is used, the ball may not rotate smoothly, causing impingement between the ball and its seat, and, thus, squeaking.

It has been attempted to meet the desired object of minimising or obviating such defects by reducing the surface tension of inks, apparently unsuccessfully.

According to the present invention, an aqueous ink comprises water and a polyhydric alcohol as an aqueous medium which contains a colourant and a lubricating additive selected from fluoro-surfactants, water-soluble silicone oils and mixtures thereof. It is preferred that the medium additionally contains an alkali metal salt of aminotrimethylenephosphonic acid. The various ingredients may be incorporated, dissolved or dispersed in the medium.

An ink of the invention may additionally comprise, as desired, a solubilising agent for a dye used as the colourant, a dispersant for a pigment used as the colourant, an anti-corrosive and/or an anti-fungal agent. Other conventional additives may also be present. An ink of the present invention can be prepared by dissolving or dispersing the various ingredients in the aqueous medium.

The aqueous medium (or "solvent" hereinafter) preferably comprises from 40 to 80 parts by weight of water and from 60 to 20 parts by weight of polyhydric alcohol. The polyhydric alcohol should be selected with regard to its evaporation, dye-solubility and blot-resistance characteristics. Preferred polyhydric alcohols are ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, butyl diglycol, thiodiglycol and glycerin.

The colourant may be a dye or pigment, or mixture thereof. Any of the dyes which are generally used in inks, for example, acid dyes, basic dyes and direct dyes, are suitable. There can be used, for example, the dyes sold under the trade names "Direct Black 19" (a direct dye) and "CI Acid Red 87" (an acid dye), both produced by Orient Kagaku Kogyo Co., Ltd. Generally, an ink of the invention comprises from 1 to 15 parts by weight of dye per 100 parts by weight of solvent.

As for the pigment, there can be employed any of the pigments which are generally used as a pigment for ink. There can be used, for example, an azo-pigment, phthalocyanine pigment, dioxazine-pigment, carbon black, titania or the like. Generally, there can be used about 1 to about 20 parts by weight of pigment per 100 parts by weight of solvent.

As for the fluoro-surfactant, there can be used, for example, one sold under the trade name "Fluorad FC 170C" which is a nonionic fluoro-surfactant produced by Sumitomo 3M Co., Ltd., or the like. Of course, it is possible to select and use the other fluoro-surfactant so as to attain the object of this invention. Generally, there can be used about 0.01 to about 1 parts by weight of fluoro-surfactant per 100 parts by weight of solvent.

As for the water-soluble silicone oil, there can be used, for example, one sold under the trade name "Toshiba Silicone Oil YF 3842" which is a copolymer of silicone and polyoxyalkylene produced by Toshiba Silicone Co., Ltd., or the like. Of course, it is possible to select and use the other water-soluble silicone oil so as to attain the object of this invention. Generally, there can be used about 0.5 to about 5 parts by weight of water-soluble silicone oil per 100 parts by weight of solvent.

As for the alkali metal salt of aminotrimethylene phosphonic acid, there can be used, for example, pentasodium aminotrimethylene phosphonate, pentapotassium aminotrimethylene phosphonate or the like. Preferably, there can be used the product sold under the trade name "KENROX #106" produced by Teikoku Kagaku Sangyo Co., Ltd. Generally, in the case that the alkali metal salt is used together with the fluoro-surfactant or water-soluble silicone oil, there can be used about 0.5 to about 10 parts by weight, preferably about 1 to about 5 parts by weight, of alkali metal salt of aminotrimethylene phosphonic acid per 100 parts by weight of solvent. The use of more than about 10 parts of the metal salt is not preferable because of the resulting increased viscosity of the ink composition.

Moreover, as occasion demands, there can be used about 3 to about 6 parts by weight of an assistant for dissolving dye, about 1 to about 5 parts by weight of a pigment dispersant and about 1 to about 2 parts by weight of the sum of anti-corrosive and antifungal agent.

The above fluoro-surfactant, water-soluble silicone oil and alkali metal salt are used to reduce the surface tension of the ink and to impart lubricating property to the ink. Particularly, the alkali metal salt can be used to further improve the lubricating property of the ink over the ink containing the fluoro-surfactant and/or the water-soluble silicone oil but not containing the salt. Although the lubricating property can be imparted by adding a phosphorus compound, the compound has a bad influence upon performance of the ink.

It should be understood that the ingredients in the present invention and amount thereof to be formulated may be appropriately selected and used so as to attain the object of the invention. Typically, there can be used the ingredients and amounts as mentioned above. With regard to the

mixture of the lubricating ingredients, there can be generally used about 0.1 to about 4 parts by weight of the combination of fluoro-surfactant and water-soluble silicone oil per 100 parts by weight of solvent, and about 0.1 to about 7 parts by weight of the combination of fluoro-surfactant, water-soluble silicone oil and alkali metal salt of aminotrimethylene phosphonic acid per 100 parts by weight of solvent.

For a better understanding of the invention, reference will now be made, by way of use example, to the accompanying drawings, in which:

Figure 1 is a sectional view of the head portion of a felt-tip pen, and

Figure 2 is a sectional view of the head portion of a ball point pen.

In Figure 1, 1 is the point of the felt-tip pen, 2 is a pen core (an axis body), 3 is a tip holder, 4 is an end portion of the felt-tip pen body and 5 is an ink absorbing and reserving member.

The pen core 2 is made from a synthetic resin such as a polyacetal resin or the like, and has a number of capillary tubes through which the ink is sucked up. The ink which has been sucked from the ink impregnated member 5 passes through the pen core 2 to the pen point 1 by capillary action. The above lubricating agent is intended to facilitate this passing of the ink.

It has been found that the lubricating agent helps the travel of the colorant due to the capillary action, even in the case that the pigment is used as colorant. Use efficiency of the impregnated ink was about 60 to about 70% while the conventional ink had a use efficiency of about 20 to 40%.

Moreover, in writing with the above felt-tip pen, friction between the pen point and the writing paper is reduced because of the lubricating agent present and thus the user can write with ease.

Accordingly, it is possible to prevent wear of the pen core and to prevent the writer from tiring. This effect is particularly remarkable in the case that the pen core is made from a rigid material such as a metal, glass, ceramic or the like.

The following reference is made with respect to Fig. 2 showing the head portion of a ball point pen.

A ball 11 fitted on the end of a tip composed of nickel-silver is held with a ball tip holder 12 composed of a metal or a synthetic resin. The tip holder 12 provides an ink hole 13 and an ink relaying member 14 is positioned adjacent to the ink hole 13. For example, the ink hole 13 can be kept in touch with the relaying member 14 or can be in part inserted therein. The ink relaying member 14 can be kept in contact with an ink impregnated member 15 or can be in part inserted into the member 15.

In writing with the above ball point pen, the ball 11 rotates and the ink which is adhered to the rotating ball 11 is transferred to the writing paper. The lubricating agent in the ink of the present invention reduces the friction induced between the ball 11 and a ball seat 16. Thus, the rotation of the ball 11 becomes a smooth and the wear of the ball seat 16 is reduced.

By using the ink composition of the invention as mentioned above, in writing with a pen no squeaking is caused between the point of the pen and the writing paper, there is no scratchiness, written characters do not become uneven in density, a good supply of the ink is continued, and there are no directional characteristics in writing, i.e., the user can make strokes in all directions with the pen with equal ease.

Below are shown formulations of the aqueous ink for writing utensils according to this invention. These are presented for explanatory purposes and are not to be considered as limiting the invention in any way.

Example 1

Solvent:	
Water	70 parts by weight
Ethylene Glycol	10 parts by weight
Diethylene Glycol	15 parts by weight
Thiodiglycol	5 parts by weight
Dye:	
"Direct Black 19"	8 parts by weight

(Trade name of direct dye produced by Orient Kagaku Kogyo Co., Ltd.)

Fluoro-surfactant:	
"Fluorad FC 170 C"	0.05 parts by weight

(Trade name of surfactant produced by Sumitomo 3M Co., Ltd.)

Example 2

Solvent:	
Water	75 parts by weight
Ethylene Glycol	10 parts by weight
Diethylene Glycol	10 parts by weight
Thiodiglycol	5 parts by weight
Dye:	
"CI Acid Red 87"	7 parts by weight

(Orient Kagaku Kogyo Co., Ltd.)

Water-soluble silicone oil:	
"Toshiba Silicone Oil YF 3842"	1.5 parts by weight

(Trade name of silicone oil produced by Toshiba Silicone Co., Ltd.)

Example 3

Solvent:	
Water	70 parts by weight
Ethylene Glycol	14 parts by weight
Diethylene Glycol	10 parts by weight
Thiodiglycol	5 parts by weight
Butyl diglycol	1 part by weight
Dye:	
"Direct Black 19"	2 parts by weight
Carbon Black:	8 parts by weight
Fluoro-surfactant:	
"Fluorad FC 170C"	1 part by weight

Example 4

Solvent:	
Water	75 parts by weight
Ethylene Glycol	10 parts by weight
Diethylene Glycol	15 parts by weight
Phthalocyanine green:	
(C.I. 74260)	10 parts by weight
Fluoro-surfactant:	
"Fluorad FC 170C"	1 part by weight

Example 5

Solvent:	
Water	70 parts by weight
Ethylene Glycol	10 parts by weight
Diethylene Glycol	15 parts by weight
Thiodiglycol	5 parts by weight
Hansa Yellow 3R:	
(C.I. 11725)	15 parts by weight
Fluoro-surfactant:	
"Fluorad FC 170C"	1 part by weight

Example 6

Solvent:	
Water	70 parts by weight
Ethylene Glycol	10 parts by weight
Diethylene Glycol	15 parts by weight
Thiodiglycol	5 parts by weight
Dye:	
"Direct Black 19"	8 parts by weight
Fluoro-surfactant:	
"Fluorad FC 170C"	0.05 part by weight
Pentasodium aminotrimethylene phosphonate:	
"KENROX #106"	2 parts by weight

(Trade name of Teikoku Kagaku Sangyo Co., Ltd.)

Example 7

Solvent:	
Water	75 parts by weight
Ethylene Glycol	10 parts by weight
Diethylene Glycol	10 parts by weight
Thiodiglycol	5 parts by weight
Dye:	
"C.I. Acid Red 87"	7 parts by weight
Water-soluble silicone oil:	
"Toshiba Silicone Oil YF 3842"	1.5 parts by weight
Pentasodium aminotrimethylene phosphonate:	
"KENROX #106"	2 parts by weight

The above ink compositions were prepared by dissolving or dispersing the dye, pigment, fluoro-surfactant, water-soluble silicone oil and alkali metal salt of aminotrimethylene phosphonic acid in the solvent comprising water and polyhydric alcohol.

In order to show the effect of the fluoro-surfactant, water-soluble silicone oil and the alkali metal salt of aminotrimethylene phosphonic acid, comparative compositions 1 to 6 were prepared by repeating the above Examples 1 to 6 except that the surfactant, the silicone oil and the metal salt were not included in the formulation.

The following Table shows the physical properties of the ink compositions of the above Examples 1 to 6 and the above Comparative Examples 1 to 6, and performance data of the ink compositions for use in a ball point pen and felt-tip pen.

Writing distance

The writing distance was determined in accordance with the procedure defined in JIS (Japanese Industrial Standard)—S6038, provided that a load of 50 g was applied with respect to the felt-tip pen and a load of 100 g was applied with respect to the ball point pen.

Use efficiency of ink

The use efficiency of the ink was calculated by the following equation:

$$\frac{A-B}{A} \times 100\ (\%)$$

A: Amount of ink reserved in the writing utensil before the writing distance test according to JIS—S6038.

B: Amount of ink remaining in the writing utensil after the writing distance test.

Example no.	Viscosity (cps)	Surface tension (dyn/cm)	Ball point pen (ball diameter: 0.7 mm)		Felt-tip pen (core of pen made of plastic, ϕ0.4 mm)	
			Writing distance (m)	Use efficiency of ink (%)	Writing distance (m)	Use efficiency of ink (%)
Ex.						
1	5.0	20	2000	60	1200	60
2	5.5	23	2000	60	1050	52
3	6	24	2000	60	1100	55
4	6.5	24	1900	55	1100	55
5	7.0	25	1900	55	1100	55
6	—	—	2200	68	—	—
Comparative Ex.						
1	5.0	40	1000	30	800	40
2	5.5	39	1200	35	800	40
3	6	38	700	20	600	30
4	6.5	39	700	20	600	30
5	7.0	40	700	20	600	30
6	—	—	950	30	—	—

Claims

1. An aqueous ink which comprises water and a polyhydric alcohol as an aqueous medium which contains a colourant and a lubricating additive selected from fluoro-surfactants, water-soluble silicone oils and mixtures thereof.

2. An ink according to claim 1, wherein the medium comprises from 40 to 80 parts by weight of water and from 60 to 20 parts by weight of polyhydric alcohol.

3. An ink according to claim 1 or claim 2, wherein the polyhydric alcohol is selected from ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, butyl diglycol, thiodiglycol and glycerin.

4. An ink according to any preceding claim, which comprises from 0.01 to 1 part by weight of fluoro-surfactant, per 100 parts by weight of the medium.

5. An ink according to any preceding claim, which comprises from 0.5 to 5 parts by weight of water-soluble silicone oil, per 100 parts by weight of the medium.

6. An ink according to any preceding claim, which comprises from 0.1 to 4 parts by weight of a mixture of fluoro-surfactant and water-soluble silicone oil, per 100 parts by weight of the medium.

7. An ink according to any preceding claim, in which the medium additionally contains an alkali metal salt of aminotrimethylene phosphonic acid.

8. An ink according to claim 7, which comprises from 0.5 to 10 parts by weight of the alkali metal salt, per 100 parts by weight of the medium.

9. An ink according to claim 7 or claim 8, which comprises fluoro-surfactant, water-soluble silicone oil and the alkali metal salt, in an amount, in total, of from 1 to 7 parts by weight, per 100 parts by weight of the medium.

10. An ink according to claim 1, substantially as described in any of Examples 1 to 7.

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